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(71) Applicant: **International Business Machines Corporation**
**Old Orchard Road**
**Armonk, N.Y. 10504 (US)**

(72) Inventor: **Lee, Kim Yang**
**36 Henry Dubois Drive, Apt. 3**
**New Paltz, NY 12561 (US)**
Inventor: **Sachdev, Krishna Gandi**
**23 Fairview Drive**
**Hopewell Junction, NY 12533 (US)**
Inventor: **Sachdev, Harbans Singh**
**23 Fairview Drive**
**Hopewell Junction, NY 12533 (US)**
Inventor: **Sooriyakumaran, Ratnam**
**15-3D Loudon Drive**
**Fishkill, NY 12524 (US)**
Inventor: **Jagannathan, Premlatha**
**4 Carolyn Way**
**Patterson, NY 12563 (US)**
Inventor: **Khojasteh, Mahmoud M.**
**21 Kendell Drive**
**Wappingers Falls, NY 12590 (US)**
Inventor: **Katnani, Ahmad Dauod**
**24 Old Farms Road**
**Poughkeepsie, NY 12603 (US)**
Inventor: **Kwong, Ranee Wai-Ling**
**31 Mina Drive**
**Wappingers Falls, NY 12590 (US)**
Inventor: **Brunsvold, William Ross**
**22 Clover Hill Road**
**Poughkeepsie, NY 12603 (US)**
Inventor: **Fahey, James Thomas**
**25 Valley Road**
**Wappingers Falls, New York 12590 (US)**
Inventor: **Hefferon, George Joseph**
**RD3 Box 43, High View Road**
**Fishkill, NY 12524 (US)**
Inventor: **Huang, Wu-Song**
**33 Ireland Drive**
**Poughkeepsie, NY 12603 (US)**
Inventor: **Wood, Robert Lavin**
**6 Argent Drive**
**Poughkeepsie, NY 12603 (US)**

(74) Representative: **Klein, Daniel Jacques Henri**
**Compagnie IBM France**
**Département de Propriété Intellectuelle**
**F-06610 La Gaude (FR)**

## (54) Environmentally stable highly sensitive acid amplifier photoresists.

(57) Acid sensitive polymeric compositions, and improved chemically amplified microlithographic resist compositions comprising the acid sensitive polymeric compositions, and methods for the preparation and use thereof are disclosed. The compositions comprise, in admixture, a polymeric binder, an acid labile moiety which provides selective aqueous base solubility upon cleavage, and a compound that generates acid upon exposure of the resist composition to imaging radiation. More particularly, the compositions have one or more acid labile ketal groups, which may be chemically linked to a polymeric resin or which may be incorporated into a separate component to form a dissolution inhibitor. The compositions exhibit reduced sensitivity to environmental contaminants when compared to known acid amplified resist compositions, and may optionally be processed without a post exposure bake step. Such compositions are especially useful in the fabrication of integrated circuit devices by microlithographic t chniques.

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Jouve, 18, rue Saint-Denis, 75001 PARIS

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The pres nt invention provides improved chemically amplified microlithographic resist compositions, polym ric components which are useful therein, and methods for the preparation and use th reof. The compositions comprise, in admixture, a compound that generates acid upon exposure of the resist composition to imaging radiation, a polymeric binder, and, either in admixture with the binder or chemically linked thereto, an acid labile moiety which provides selective aqueous base solubility of the mixture upon cleavage. The invention is particularly related to compositions having an acid labile moiety comprising a ketal functional group. Such compositions are especially useful in the fabrication of integrated circuit devices by microlithographic techniques.

In the fabrication of high density integrated circuits having sub micron dimensions, the coating, exposure, and development of a photoresist layer are particularly critical processing steps, and must be accomplished within close processing tolerances. For example, it is important to control the linewidth of the imaged and developed photoresist so that any deviation from the nominal design linewidth is small, typically less than ±10%. The profiles of the imaged and developed photoresist structures must be straight with vertical sidewalls. Photospeed must be such that the required exposure dose is less than about 100 mJ/cm$^2$ and preferably less than about 25 mJ/cm$^2$. Moreover, and in part because the exposure of individual substrates is typically accomplished in a serial manner, whereas development is typically accomplished in a batch manner, it is desirable to use photoresists which are tolerant of a variable time delay between the exposure and development steps, and also between each of any intervening steps. In sub micron lithography, the use of acid amplified resists has become favored due to the high photospeed of such compositions.

The use of acid amplified resist compositions is well known in the art. Such resist compositions are especially useful in conjunction with deep UV (180-300 nm), e-beam, and X-ray exposure tools, in light of their high photospeed characteristics. The following references illustrate the state of the pertinent art.

U.S. Pat. No. 3,779,778 to Smith, et al., discloses photosolubilizable compositions comprising a water insoluble compound having acid labile groups and a photosensitive acid progenitor. Acid labile groups which are disclosed include acetal groups.

U.S. Pat. No. 4,491,628 to Ito, et al., discloses chemically amplified photoresist compositions comprising a photosensitive acid progenitor and a polymeric component having acid labile groups pendent therefrom, wherein the acid labile groups are tert-butyloxycarbonyloxy groups.

U.S. Pat. No. 4,946,759 to Doessel, et al., discloses a positive tone, radiation sensitive composition comprising a photosensitive acid generator, and an acid cleavable compound which may be a carboxamide acetal or a polymeric compound having recurrent acetal groups in polymer main chain.

U.S. Pat. No. 4,946,760 to Elsaesser discloses a radiation sensitive composition comprising a photosensitive acid generator, and an acid cleavable compound which may be a polymeric compound having recurrent acetal groups in polymer main chain.

European Application EP 0 520 642 A discloses a resist composition comprising a photosensitive acid progenitor and a polymeric component having acid labile groups pendent therefrom, wherein the acid labile groups are acetal or ketal groups.

Japanese Patent Kokai No. 02-248,953 (1990) discloses a three component photosensitive composition comprising an alkali soluble polymeric resin, a photosensitive acid generator, and an acid cleavable tetrahydropyranyl substituted phenol.

Jiang and Bassett have described the preparation and use of chemically amplified deep UV photoresists comprising a photosensitive acid generator and a polymeric component having acid labile acetal groups pendent therefrom. Y. Jiang and D. Bassett, Chemically Amplified Deep UV Photoresists Based On Acetal-Protected Poly(vinylphenols), Proc. Amer. Chem. Soc., Div. Polym. Mater. Sci. Eng., 66, 41 (1992).

Hayashi, et al., have previously described the preparation and use of chemically amplified deep UV photoresists comprising a photosensitive acid generator and acetal substituted poly(hydroxystyrenes). Hayashi, et al., Tetrahydropyranyl and Tetrahydrofuranyl Protected Polyhydroxystyrenes in Chemical Amplification Resist Systems for KrF Excimer Laser Lithography, Proc. Amer. Chem. Soc., Div. Polym. Mater. Sci. Eng., 61, 417, (1989); Hayashi, et al., Polyvinylphenols Protected With Tetrahydropyranyl Group in Chemical Amplification Positive Deep UV Resist Systems, SPIE, Adv. Resist Technol. and Process. VIII, 1466, 377, (1991); S. Hesp, N. Hayashi, and T. Ueno, Tetrahydropyranyl and Tetrahydrofuranyl Protected Polyhydroxystyrene in Chemical Amplification Systems, J. Appl. Polym. Sci., 42, 877, (1991).

Although chemically amplified photoresist compositions are favored for sub micron lithography, those chemically amplified photoresists which are bas d on tert-butyl ethers, esters, and carbonates are particularly sensitive to environmental contaminants and thus often require a overlaying top coat as a protective barrier layer. Furthermore, such compositions are not tolerant of variable or lengthy delays between exposure and the post exposure bake (PEB) required for such compositions, as the photogenerated acid species may diffuse from the exposed region of the resist or may be consumed by adverse contact reactions.



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Chemically amplified photoresist compositions bas d on acid labile groups comprising acetals often give rise to unpredictable results. In particular, photoresist components comprising an acetal moiety designed to produce a hydroxylic moiety imparting base solubility to the resist typically yield aldehydes upon acid catalyzed cleavage or hydrolysis. In turn, such aldehyde species may lead to resist crosslinking by means of aldol condensation reactions under the influence of heat or radiant energy from the exposing radiation source. Thus, many such acetal based resists unpredictably demonstrate both positive tone and negative tone behaviors. Furthermore, known photoresist compositions based on acetal acid labile groups exhibit a cleavage reaction rate of some nominal value in the exposed regions even at ambient temperature, which reaction rate is accelerated during a PEB step. The cleavage reaction may also continue at a slow rate following PEB and prior to development. If such compositions are processed without the use of a PEB, competing contact reactions or reactions with environmental contaminants slow and interrupt the cleavage reaction prior to completion of acetal cleavage sufficient to render the composition differentially soluble, thus acceptable relief images can not be obtained. If such compositions are processed with the use of a PEB, the degree of completion of the cleavage reaction varies highly depending upon the variation in delay time between the exposure step and the PEB step, and also depending upon the remaining, unconsumed acid present in the resist at the commencement of the PEB step. For these reasons, the results are unpredictable. Thus, there is a need for improved chemically amplified photoresist compositions which are not subject to adverse reactions with environmental contaminants and which are tolerant of variable or lengthy delays between exposure and the post exposure bake step, if any, or between the PEB step and development.

According to the invention, improved chemically amplified microlithographic resist compositions, polymeric components which are useful therein, and methods for the preparation and use thereof are disclosed. The compositions comprise, in admixture, a polymeric binder, an acid labile moiety which provides selective aqueous base solubility upon cleavage, and a compound that generates acid upon exposure of the resist composition to imaging radiation. More particularly, the compositions have one or more acid labile ketal groups, which may be chemically linked to a polymeric resin or which may be incorporated into a separate component to form a dissolution inhibitor. The compositions exhibit reduced sensitivity to environmental contaminants when compared to known acid amplified resist compositions, may be processed without a post exposure bake step, and have equivalent or better photospeed than known compositions.

The present invention provides novel compositions which are improved chemically amplified microlithographic resists. The compositions comprise, in admixture, a compound that generates acid upon exposure of the resist composition to imaging radiation, a polymeric binder, and, either in admixture with the binder or chemically linked thereto, an acid labile moiety which provides selective aqueous base solubility of the mixture upon cleavage. The invention is particularly related to compositions having an acid labile moiety comprising a ketal functional group. The compositions are useful in conjunction with lithographic exposure systems using any of electron beam, ion beam, ultraviolet, or x-ray radiation. The artisan will appreciate that other radiation sources known in the art will also be useful. The compositions are particularly suitable for patternwise exposure with deep UV radiation. Deep UV is considered to be ultraviolet light having a wavelength in the range from about 180 nm to about 300 nm.

The compositions of the invention are said to be chemically amplified. By this is meant that one photon or energetic particle is absorbed by the acid generator which produces one acid molecule that subsequently can cause up to about a thousand chemical events, or individual cleavage reactions of the acid labile groups, to take place. The acidic moiety acts as a catalyst, because the acid is regenerated after each of many individual reactions. The generation of acid from the radiation sensitive acid generator does not require heat, however, most known chemically amplified resists require a post-exposure bake (PEB) of one to two minutes in length to complete the reaction between the acid moiety and the acid labile component. During this time, acid diffusion in the film can cause an undesirable effect if acid moieties migrate into unexposed regions or are consumed by contaminants prior to reacting with the acid labile component. However, it is particularly noted that the compositions of the present invention undergo facile acid catalyzed cleavage of the ketal group at room temperature, and thus, optionally do not require a PEB step in processing. This is decidedly advantageous in controlling image size and quality.

The compositions of the invention are particularly useful for microlithography in that image size is not particularly sensitive to changes in post-exposure bake temperature or delay time. A change of less than about ± 2 nm in feature size per change in °C of PEB temperature is observed in printing images. Additionally, a change of less than about ± 10% in feature size having a nominal line width of 0.35 μm was observ d between substrates exposed to deep UV with a .37NA lens, processed with minimal delay time between exposure and PEB temperature and those substrates processed with a 24 hour delay time in ambient condition storage. Furthermore, the compositions of the invention are not sensitive to the deleterious effects of environmental contaminants, such as air-borne vapors of organic bases, NMP vapor, and the volatile products of common ma-



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terials present in a fabrication facility such as paints, glues, and caulking materials. This is especially useful in state-of-the-art semiconductor manufacturing where printing sub-micron imag s necessitat s a tight linewidth tolerance with respect to the target dimension. In a manufacturing process, the linewidth tolerance is usually about ± 10% of the nominal dimension.

The present invention is directed to compositions in which the acid labile group is a ketal group. The acid labile compound comprising a ketal moiety may be chemically linked to a component of the resist composition which functions as a dissolution inhibitor and is in physical admixture with a film forming polymer having recurrent hydroxyl groups and further in admixture with a radiation sensitive acid generating compound. In alternative embodiments, the acid labile group comprising a ketal moiety may be chemically linked to the film forming polymer by means of the ketal group wherein one or more of the ketal oxygens is derived from a polymeric hydroxyl group. Such polymeric species may be prepared by the chemical reaction between film forming polymers having recurrent hydroxyl groups and ketal progenitors including, without limitation, substituted vinyl ethers, and orthoesters. Such polymeric species may also be prepared by the transetherification reaction between a ketal and a polymer having recurrent hydroxyl groups chemically linked thereto. Where the ketal moiety is incorporated by chemical reaction with one or more of the recurrent hydroxyl groups, the hydroxyl groups of the polymeric product may be partially or fully substituted. The degree of substitution may be in the range from about 5 to 8% to about 100%.

The present invention also contemplates additional, alternative embodiments wherein the ketal moiety is chemically linked to a suitable host polymer having recurrent hydroxyl groups, and wherein the chemical linkage does not contain one of the said recurrent hydroxyl groups. The skilled artisan will appreciate that where the appropriate solubility properties are achieved, the ketal moieties may, for example, be chemically linked to, and dependent from, the polymer backbone, but separate from the recurrent hydroxyl groups. Similarly, the ketal moiety may, for example, comprise a portion of the polymer chain. Furthermore, in additional, alternative embodiments the ketal moiety may be chemically linked to alternative functional groups, including without limitation, carboxylates, sulfonamides, and other functional groups known in the art. Finally, in yet another alternative embodiment contemplated by the present invention, the ketal moiety may be chemically linked to the acid generating compound. The foregoing contemplated embodiments are intended to be merely illustrative of alternative embodiments within the scope of the invention and not to be limiting thereto.

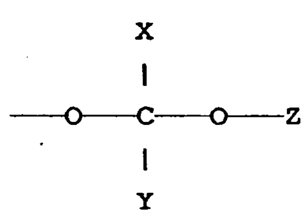
The acid labile compounds comprising a ketal moiety which are useful in the present invention may be further characterized as imparting the property of differential solubility to the exposed, as compared to the unexposed, areas of a resist film formed from the compositions of the invention. By differential solubility is meant those portions of the film which have been exposed to imaging radiation become selectively soluble in aqueous base developers, whereas those portions of the resist compositions which have not been exposed to imaging radiation remain relatively less soluble in the aqueous base developers. The artisan will appreciate that the presence of the ketal moiety renders a portion of the film relatively less soluble in developer, and that the absence of the ketal moiety, or the cleavage products thereof, render a portion of the film relatively more soluble in developer.

Additionally, the acid labile compounds comprising a ketal moiety which are useful in the present invention may be characterized as having sufficient reactivity towards the acid derived from the acid generating compound so as to result in the cleavage of at least a portion of the ketal groups upon exposure to such acid.

Furthermore, the acid labile compounds comprising a ketal moiety which are useful in the present invention may be additionally characterized as being soluble in a coating solvent.

Examples of acid labile compounds comprising a ketal moiety which are useful in the present invention include, without limitation, polymers comprising a ketal group, substituted and unsubstituted ketal compounds and substituted and unsubstituted functional groups comprising a ketal and having less than about 40 carbons, provided however, that such polymers, compounds, and functional groups have the requisite reactivity with acids and solubility properties.

Examples of preferred acid labile compounds comprising a ketal moiety include compounds having the form





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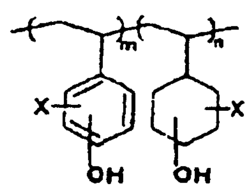
wherein X, Y, and Z, ar selected, independently, from the group consisting of non-bridging alkyl, aryl, alicyclic, and O-heterocyclic groups, and bridging groups comprising 2 to 8 carbons between any two of X, Y, and Z. Examples of more preferred acid labile compounds comprising a ketal moiety include compounds wherein the ketal moiety is selected from the group consisting of 2-(2-methyl-tetrahydrofuranyl)oxy, 2-(2-methyl-tetrahydropyranyl)oxy, 1-(1-methoxycyclohexyl)oxy, 2-(2-methoxypropyl)oxy, 4-(4-methoxy-tetrahydropyranyl)oxy, and (1-phenoxy-1-phenylethyl)oxy. An example of a most preferred acid labile compound comprising a ketal moiety is a compound comprising the 2-(2-methoxypropyl)oxy group.

The polymeric binders which are useful in the present invention include film forming polymers having recurrent hydroxyl groups chemically linked thereto and derivatives thereof. Polymeric binders which are useful in alternative embodiments are film forming polymers having recurrent hydroxyl groups chemically linked thereto and derivatives thereof wherein at least a portion of the film forming polymer hydroxyl groups are O-substituted with an acid labile compound comprising a ketal moiety. The degree of O-substitution may be in the range from about 5 to 8% to about 100%. Polymeric binders which are useful in additional alternative embodiments are film forming polymers having recurrent hydroxyl groups chemically linked thereto and derivatives thereof which polymers further comprise an acid labile compound comprising a ketal moiety.

The polymeric binders which are useful in the present invention are further characterized as imparting the property of differential solubility as previously described above. That is, the polymeric compositions are selected so that those portions of the resist compositions which have been exposed to imaging radiation become selectively soluble in aqueous base developers, whereas those portions of the resist compositions which have not been exposed to imaging radiation remain relatively less soluble in the aqueous base developers.

Examples of preferred polymers include hydroxyaromatic polymers which are the condensation reaction product of a substituted or unsubstituted phenol with an aldehyde. By hydroxyaromatic polymers is meant those polymeric compositions comprising a substituted or unsubstituted phenol, naphthol, or congeneric groups having a hydroxyl group directly bonded to an aromatic ring, wherein the aromatic ring may be pendent from the polymeric backbone or may be in the polymeric chain. Preferred polymers also include polymers or copolymers derived from a substituted or unsubstituted hydroxystyrene, by which is meant that the polymers or copolymers have an aliphatic or partially aliphatic polymer backbone and have hydroxyaromatic groups pendent therefrom. Examples of more preferred polymers include novolak resins, and polymers which are the condensation reaction product of formaldehyde with phenol or an alkylphenol, and polyhydroxystyrene.

In an alternate embodiment, the polymer may be a copolymer derived from a substituted or unsubstituted hydroxystyrene and an olefinically substituted cyclic alcohol. In an alternate preferred embodiment, the polymer may be poly(hydroxystyrene-co-vinyl cyclohexanol) which is described in U.S. Patent No. 5,128,232 to Thackeray, the disclosure of which is incorporated herein by reference. The poly(hydroxystyrene-co-vinyl cyclohexanol) has the form



where X is, independently, a hydrogen or an alkyl group having 1 to 8 carbons, and m is in the range of about 0.8 to 1, and n is in the range of about 0 to 0.2.

The radiation sensitive acid generating compounds which are useful in the present invention include, without limitation, metallic, metalloid, and non-metallic onium salts of which examples are described in U.S. Patent No. 4,102,687, aryl sulfonates including without limitation, tris-pyrogallol sulfonates and anthracene-2-sulfonates such as 9,10-diethylanthracene-2-sulfonate, 2-nitrobenzyl esters, beta-ketosulfones, disulfones, arylsulfonyl- alpha-keto- and alpha-carboxyl- diazomethanes, and precursors of substituted and unsubstituted sulfonic acids, including, without limitation, oxime sulfonates as described in EP 0 361 907 to Hoechst Celanese Corporation, and in the publication of Shirai, et al., "Synthesis and Photo-Induced Dissolution of Polymers Bearing Imino Sulfonate Groups," J. Polym. Sci. A, 27, 325 (1989), and N-hydroxyimides of the type described in U.S. Patent No. 4,371,605. Preferred radiation sensitive acid generators include the acid progenitors described in copending U.S. Patent Application Serial No. 07/968,120 filed 10/29/92, entitled "Chemically Amplified Photoresists Comprising Non-Metallic Photosensitive Acid Generators" (attorney docket number FI9-88-046X) the disclosure of which is incorporated herein by reference. Examples of preferred radiation sensitive acid generators disclosed in the cited application include N-(trifluoromethylsulfonyloxy)-bicyclo-[2.2.1]hept-5-en -2, 3-



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dicarboximide (MDT), N-(trifluoromethylsulfonyloxy)-nitronaphthalimides, N-(trifluoromethylsulfonyloxy)-4-halonaphthalimides, N,N'-bis(camphorsulfonyloxy)-3,4,9,10-perylenet tracarboxdiimid , N- (trifluoromethylsulfonyloxy)-7-oxabicyclo-[2.2.1]hept-5-ene-2,3-dicarboximide, N-(trifluoromethylsulfonyloxy)-succinimide, N,N'-bis-(trifluoromethylsulfonyloxy)-(3-methyl-4,5-imido-cyclohex-3-enyl)-succinimide,N-(trifluoromethyl-sulfonyloxy)-diphenylmaleimide, di-[N-(trifluoromethylsulfonyloxy)-phthalimidyl]-ether,bistrifluoromethyl-bis-N,N'-(trifluoromethylsulfonyloxy)-phthalimidylmethane,N-(camphorsulfonyloxy)-naphthalimide,N-(camphorsulfonyloxy)-nitronaphthalimides, and the corresponding tosyl-, brosyl-, fluoro- and perfluorobenzenesulfonyloxy-, nitrobenzenesulfonyloxy-, and halobenzenesulfonyloxy- analogs thereof. The practitioner will understand that other radiation sensitive acid generators which are known in the art are anticipated to be useful.

In alternative embodiments, other radiation sensitive acid generating compounds which are useful in the present invention include 2-diazo-1-naphthoquinone-4-sulfonic acid esters, 2-diazo-1-naphthoquinone-5-sulfonic acid esters, and mixtures and combinations thereof. It is particularly noted, however, that compositions comprising a 2-diazo-1-naphthoquinone-5-sulfonic acid ester as an acid generating species typically require a post exposure bake step during lithographic processing.

In additional alternative embodiments, other radiation sensitive acid generating compounds which are useful in the present invention include polymerically bound radiation sensitive acid generators including polymers having hydroxyl groups wherein at least a portion of the hydroxyl groups are O-substituted with substituted or unsubstituted diazoacetoacetate ester groups. In an additional alternative embodiment, the acid generator may be a polymerically bound bis-keto diazomethane.

The polymeric compositions of the present invention may be dissolved in various solvents to provide a composition which is useful for forming thin films. Solvents may be esters, ethers, ketones, alcohols or other resist solvents known in the art. Particular examples of solvents include, without limitation, alkoxy alkanols such as methoxypropanol, Γ-butyrolactone, ethyl lactate, acetate and propionate esters, tetrahydrofurfural alcohol, or combinations thereof. The preferred solvents are acetate esters and ethyl lactate.

Typical liquid photoresist compositions will have up to about 50% solids. In embodiments wherein the acid labile moiety is a separate component from the polymeric binder component, the typical proportion of acid labile component to binder may be in the range from about 10:90 to about 40:60.

In embodiments wherein the acid labile moiety is chemically linked by means of O-substitution to at least a portion of the film forming polymer hydroxyl groups, the degree of substitution of hydroxyl groups may be in the range from about 5 to 8% to about 100%. In such embodiments the typical proportion of acid generator to acid labile moiety may be in the range from about 0.1:99.9 to about 30:70.

In yet another alternative embodiment, traces of a surfactant may also be added to the resist compositions.

In yet another alternative embodiment, a dye may also be added to the resist compositions. The dye may be useful for modifying the properties of the resist, or may be useful as an energy transfer means. Dyes may include, without limitation, 9-anthracenemethanol, 9-phenoxymethylanthracene, 9,10-diphenylanthracene, substituted phenanthracenes and substituted biphenyls, 4-phenylazoresorcinol and dyes related thereto, crystal violet base, and dyes selected from the coumarin class of dyes.

In yet another alternative embodiment, a residual acid scavenger may be added to the resist compositions. Examples of residual acid scavengers include tetraalkylammonium hydroxides, tetraalkanol ammonium hydroxides, dimethylaminopyridines, and ethylene oxide / propylene oxide block copolymer surfactants.

Additional uses and embodiments of the present invention will become apparent to the skilled artisan upon reading the following detailed examples.

## Example 1

Synthesis of poly(p-hydroxystyrene-co-p-(2-(2-methoxy)-propyloxy)styrene (PHMOP)

250g of polyhydroxystyrene (available from Hoechst, 8,100 Mw) was heated at 60 °C in vacuum oven overnight to remove water. It was then dissolved in 750 ml of anhydrous tetrahydrofuran (THF) in a 2 liter round bottom flask, and the flask and contents were immersed into a dry ice/acetone bath. 46.46g (0.3 equivalents based on polyhydroxystyrene) of methoxypropene was added to the solution with stirring. After mixing, 53mg of p-toluene sulfonic acid was added. The reaction was allowed to continue at reduced temperature for one hour, then the bath was removed and the reaction was continued for another one hour at room temperature. To quench the reaction, 30ml of concentrated ammonium hydroxide solution was added to the polymer solution. The solid polymer product was precipitated by dripping the polymer solution into water containing ammonium hydroxide (16ml in 3000ml water). After filtration and washing with water (or alternatively, water containing ammonium hydroxide solution), the solid was dried under nitrogen and suction for 2 to 3 hours. Finally, the polymer solid was dried in vacuum overnight at room temperature. The polymer was then analyzed with NMR, IR and TGA. The data obtained ar summarized below:



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Table 1

Summary of NMR & TGA data from different lots:

| Lot | THF/PHS (NMR) | MOP/PHS (NMR) | (THF+MOP)/PHS (NMR) | TGA (THF+MOP)/PHS |
|---|---|---|---|---|
| #1 | 13.4 | 21.8 | 35.2 | 33.9 |
| #2 | 16.2 | 21.5 | 37.8 | 39.1 |
| #3 | 16.8 | 16.7 | 33.5 | 30 |
| #4 | 7.5 | 15.8 | 23.3 | 28.5 |
| #5 | 10.1 | 14.0 | 24.1 | 26.5 |

Infrared spectra of all the lots have two absorption peaks at 1068 and 1134 cm -1 which are the characteristics of ketal functionality on the polymer. The peak heights are proportional to the MOP/PHS ratio. In the synthesis of lot #3, the polyhydroxystyrene used was only 60g and the sample was dried under a nitrogen stream at 70 to 80 °C overnight before reaction. Both lot #3 and #5 used HPLC grade THF instead of anhydrous THF from Aldrich. In lot #4, the methoxy propene was from Jansen (92% pure) and was purified through vacuum distillation. The weight of methoxy propene used in lot #4 was 45.06g. In lot #3 and #5, the molecular weight of the PHOST is 8,600.

Example 2

Synthesis of PHMOP having differing degrees of substitution.

Using the synthetic procedure of example 1, the amount of methoxypropene was varied to obtain PHMOP having varying degrees of substitution. The results are shown in Table 2 below:

Table 2

Summary of NMR & TGA data from different lots:

| Lot | Reactant (Molar %) | THF/PHS (NMR) | MOP/PHS (NMR) | (THF+MOP)/PHS (NMR) | TGA (THF+MOP)/PHS |
|---|---|---|---|---|---|
| #6 | 35% | 13.3 | 19.3 | 32.6 | 35 |
| #7 | 40% | 12.9 | 23.4 | 36.3 | 40 |
| #8 | 50% | 14.3 | 27.4 | 41.7 | 50 |

The reaction of lot #6 and #7 is similar to that of #4 in example 1 and the reaction of #8 is similar to that of #3. In lot #8 the molecular weight of the PHOST is 8,600.



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Example 3

Synthesis of PHMOP with higher molecular weight PHOST at room temperature.

24g of PHOST (Hoechst, 11,000 Mw) in 150 ml of THF was stirred until the solid polymer was completely dissolved, and then a large quantity of anhydrous sodium sulfate was added to remove water. The mixture was stirred for two hours, then 5g of 2-methoxypropene was then added to the mixture. After stirring for a few minutes, 100mg of p-toluene sulfonic acid was added and the reaction continued for one hour. The reaction was quenched with lml of N-methylmorpholine. The mixture was filtered through a celite filter bed to remove sodium sulfate. The solid polymer was precipitated by dripping the filtered solution into water containing ammonium hydroxide (5 ml concentrated ammonium hydroxide in 1600 ml of water). The solid was filtered and dried under vacuum.

Example 4

Synthesis of PHMOP from Maruzen PHOST

10.2g of PHOST (available from Maruzen, containing 10% of vinyl cyclohexanol copolymer) was dissolved in approximately 40ml of THF containing solid anhydrous sodium sulfate. The procedure of Example 3, except with 4g 2-methoxypropene, and 30mg p-toluene sulfonic acid monohydrate was used. The reaction was quenched with 3ml of concentrated ammonium hydroxide. The final weight of the product was 11.8g.

Example 5

Synthesis of PHMOP in ethyl acetate using ion exchange resin.

36g of PHOST (Hoechst, 8,600 Mw) in 180 ml of ethyl acetate was stirred until the solid polymer was completely dissolved, and then 11.2g of 2-methoxypropene was added to the solution. After stirring for a few minutes, 750mg of Amberlyst 15 acidic ion exchange resin was added and the reaction was continued for one hour. The resin was then filtered out with a 0.2 μm filter. The filtered solution was dried using rotary evaporation to give 43g of a solid polymer product.

A resist was formulated with 3% triphenylsulfonium triflate (TPS), 0.24% tetrabutylammonium hydroxide (TBAH), and the polymer synthesized above dissolved in PMA to give a total solid content of 20%. The resist was coated on a HMDS primed silicon wafer and baked at 100 deg C for 120 sec on a hot plate. The resist had a film thickness of about 8.53 KÅ. The coated wafer was exposed to a DUV radiation through a chrome mask on Canon 0.37NA Excimer Laser Stepper at 248nm and received a dose of 8.5 Mj/cm$^2$. The exposed wafer is then developed in 0.154 N aqueous TMAH for 75 seconds. The resist yielded 0.50 μm positive tone images. The film thickness loss was only 360 Å.

Example 6

Synthesis of PHMOP at room temperature.

20g (0.165 M) poly(4-hydroxystyrene) (Hoechst, 8,200 Mw) was dissolved in 75 ml of anhydrous THF. 5-6 mg of p-toluene sulfonic acid was added as catalyst. After 4.79 g (0.066 M) of 2-methoxypropene was added in one portion, the reaction mixture was stirred at room temperature for 3 hours. 2.6 mg of ammonium hydroxide was then added to neutralize the acid catalyst. The solution was then added dropwise to 800 ml of deionized water to precipitate the polymer. The polymer was filtered, washed several times with deionized water and dried in a vacuum oven. The NMR data of the polymer showed MOP/PHS = 17.3 and THF/PHS = 16.4.

A resist was formulated with 0.7% TPS and 0.14% TBAH in the polymer synthesized above, and dissolved in PMA to give a total solid content of 20%. The resist was coated on a HMDS primed silicon wafer and baked at 100 deg C for 120 sec on a hot plate. The resist had a film thickness of about 1.2 μm. The coated wafer was exposed to a DUV radiation through a chrome mask on Canon 0.37NA Excimer Laser Stepper at 248nm and received a dose of 36 mJ/cm$^2$. The exposed wafer is then developed in 0.14 N aqueous TMAH for 120 seconds. 0.50 μm positive images with vertical profiles were obtained.

Exampl 7

Synthesis of PHMOP using HC1.

20 g (0.165 M) of poly(4-hydroxystyrene) (Hoechst, 8,200 Mw) was dissolved in 75 ml of anhydrous THF. The solution was cooled in an ice bath to 0 °C. Two drops of concentrat d HCl was added to the solution. After 4.79 g (0.066 M) of 2-methoxypropene was added, the mixture was stirred at 0 °C for one hour followed by



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one hour at room temperature. Ammonium hydroxide (2.6 ml) was added to neutralize the acid and the resulting solution was added dropwise to 800 ml of deionized water to precipitate the polymer. The polymer was filtered and washed thoroughly with deionized water and dried in a vacuum oven. The NMR data of the polymer showed MOP/PHS = 8.9 and THF/PHS = 25.8.

A resist was formulated with 0.7% TPS and 0.14% TBAH in the polymer synthesized above and dissolved in PMA to give a total solid content of 20%. The resist was coated on a HMDS primed silicon wafer and baked at 100 deg C for 120 sec on a hot plate. The resist had a film thickness 1.12 μm. The coated wafer was exposed to a DUV radiation through a chrome mask on Canon 0.37NA Excimer Laser Stepper at 248nm and received a dose of 30 mJ/cm$^2$. The exposed wafer was then developed in aqueous tetramethyl ammonium hydroxide (0.15N TMAH) for 60 seconds. Reasonable images were resolved with film thickness loss of 0.14 μm.

## Example 8

Synthesis of PHMOP with excess 2-methoxypropene

20g (0.165 M) poly(4-hydroxystyrene) (Hoechst, 8,200Mw) was dissolved in 75 ml of anhydrous THF. 5-6 mg of p-toluene sulfonic acid was added as a catalyst. After the solution was cooled in an ice bath, 13 g (0.18 M) of 2-methoxypropene was added and the solution was stirred at 0 °C for one hour and at room temperature for one hour. The reaction was quenched with 2.6 ml of ammonium hydroxide. The solution was added dropwise to 800 ml of deionized water and the precipitated polymer was filtered, washed thoroughly with deionized water and dried in vacuo. The NMR data of the polymer showed MOP/PHS = 49.6 and THF/PHS = 12.9.

A resist was formulated with 0.7% TPS and 0.14% TBAH in the polymer synthesized above, and dissolved in PMA to give a total solid content of 20%. The resist was coated on a HMDS primed silicon wafer and baked at 100 deg C for 120 sec on a hot plate. The coated wafer was exposed to a DUV radiation through a chrome mask on Canon 0.37NA Excimer Laser Stepper at 248nm and received a dose of 34 mJ/cm$^2$. The exposed wafer was then developed in aqueous tetramethyl ammonium hydroxide (0.14N TMAH) for 80 seconds to obtain 0.35 μm positive images.

## Example 9

Synthesis of methoxypropyl substituted poly(4-hydroxybenzylsilsesquioxane).

4g (0.025 M) of poly(4-hydroxybenzylsilsesquioxane) was dissolved in 50 ml of ethyl acetate and cooled in an ice bath. After 0.15 g of Amberlyst-15 ion exchange resin was added to the solution, 1 g (0.014 M) of 2-methoxypropene was added and the solution was stirred at 0 °C for one hour and at room temperature for 30 minutes. The solution was filtered and the solvent was removed by rotary evaporation. The residue was dried in a vacuum oven.

A resist was formulated with 2% TPS and the methoxypropyl protected poly(4-hydroxybenzylsilsesquioxane) as synthesized above in PMA to give a total solid content of 20%. The resist was coated on hardbaked novolak underlayer and exposed to Deep-UV radiation On Canon 0.37NA Excimer Laser Stepper at 248 nm. Images down to 0.4 μm had been resolved at 25-30 mJ/cm$^2$.

## Example 10

Synthesis of 4,5-dihydro-2-methylfuran substituted polyhydroxystyrene.

24g of polyhydroxystyrene (8,600 M.W.) was heated to about 80 °C in a round bottom flask under a nitrogen stream overnight to remove residual water from the polymer. The dried sample was then dissolved in approximately 70-80 ml of THF. 8.8 g of 4,5-dihydro-2-methylfuran was then added to the solution. The solution was stirred vigorously for a few minutes, then about 45 mg of p-toluenesulfonic acd monohydrate was added. The solution started to warm, and was then emerged into a water bath. The reaction was allowed to continue for 100 minutes, then quenched with 4 ml of concentrated ammonium hydroxide. The polymer was allowed to precipitate out of the dilute ammonium hydroxide-water solution. The polymer was filtered, washed and then dried under vacuum for more than 18 hours. The final weight of the polymer was approximately 33g. The IR spectrum of above synthesized polymer shows two new peaks between 1000 cm-1 and 1150 cm-1, which indicates the existence of ketal protecting group on the polymer.

A resist formulation was obtained with the following compositions: 0.18% tetrabutylammonium hydroxide, 1.5% triphenyl sulfonium triflat and the 4,5-dihydro-2-methylfuran substituted polymer described above to make up 22% solids in PMA. It was spin coated on silicon wafer to give a thickness around 10.6 KÅ. It was then exposed at Oriel tool with around 30 mj. After developing in 0.1 N TMAH for 40s, the image was cleared out with no significant thinning. Another wafer with resist thickness around 9.38 KÅ was exposed in the excimer



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laser system at 25 mJ and d veloped in 0.105N TMAH (diluted from MF321). Th final thickness was 8.11 KÅ. The image was clear d out. All th above experiments were carried out without post exposure bake. The resist always generated latent image right after exposure which indicates that the rate of chemical amplification is very high.

Example 11

Synthesis of methoxypropyl protected Novolak polymer

The synthetic procedure was the same as example 1. In the reaction, the amount of meta-cresol novolak was 60g, the amount of THF used was 200 ml, the amount of 2-methoxypropene was 72g, and the amount of p-toluene sulfonic acid was 12.7 mg. The reaction was carried out at -78 °C for one hour followed by one and half hour at room temperature. It was then quenched with 10 ml of concentrated ammonium hydroxide and worked out the same way as example 1. The final dried sample shows nearly 100% protection on all the hydroxyl group of the novolak polymer according to the NMR data.

A resist formulation was obtained with the following compositions: 0.14% TBAH, 0.7% triphenyl sulfonium triflate and methoxypropyl substituted novolak as synthesized above, to make up 20% solids in PMA. It was spin coated on silicon wafer baked at 100° for 60s to give a thickness around 4.4 KÅ. It was then exposed on an Oriel tool at about 80 mJ. A sharp latent image developed right after exposure. It was post exposure baked at 80 °C for 60s. After developing in 0.54 N TMAH for 5 minutes, the image was cleared out with no resist thinning at all. When the resist was exposed with 20 mj, the develop time needed was much longer than 5 minutes. There was also no film thickness loss in this experiment.

Example 12

Synthesis of methoxypropyl substituted 6F-bisphenol A.

3.36 g (0.01 M) of 6F-bisphenol A was dissolved in 25 ml of anhydrous THF and the mixture was cooled to 0 °C in an ice bath. After 0.15 g of Amberlyst-15 was added as a catalyst, 2.5 g (0.035 M) of 2-methoxypropene was added, and the mixture was stirred for one hour at 0 °C and 30 minutes at room temperature. The solution was then filtered to remove the ion exchange resin and the solvent was removed by rotary evaporation. The sticky solid was dried thoroughly under vacuum.

Example 13

Synthesis of methoxypropyl substituted 1,1,1-tris(4-hydroxyphenyl)ethane

3.06 g (0.01 M) of 1,1,1-tris(4-hydroxyphenyl)ethane was dissolved in 50 ml of ethyl acetate and cooled in an ice bath. 0.1 g of Amberlyst-15 and 4.0 g (0.05 M) of 2-methoxypropene were added, and the mixture was stirred at 0 °C for one hour and at room temperature for 30 minutes. The solution was filtered to remove the ion exchange resin and the solvent was removed by rotary evaporation. The viscous residue was dried thoroughly under vacuum.

Example 14

Synthesis of polymer bound diazoacetoacetate.

The above polymer was synthesized by the following two step process.

(a). 12.1 g (0.1 M) Poly(4-hydroxystyrene) was dissolved in a cyclopentanone/toluene (40 ml/20 ml) solvent mixture. 14.2 g (0.09 M) t-Butyl acetoacetate was added dropwise over 5 minutes and the mixture was then refluxed overnight. The solvent mixture, along with the t-butyl alcohol generated by the transesterification reaction, was removed by distillion under vacuum and the residue was precipitated into water, filtered and dried to give the acetoacetylated polymer.

(b). 12 g of the acetoacetylated polymer from step (a) was dissolved in 20 ml acetonitrile and cooled in an ice bath. 6 g Triethylamine was added, followed by 12 g p-toluenesulfonyl azide, and the mixture was stirred at 0 °C for 1 hour and at room temperature for 3 hours. The solvent was then removed by rotary evaporation. The residue was redissolved in aceton and precipitated into deionized water containing approximately 5% KOH. The precipitate was filtered, washed several times with wat r and dried to yield the polymer bound diazoacetoacetate.



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## Example 15

Lithographic dose vs. photo acid generator loading

Three sets of resists were formulated with PHMOP (synthesized in Exampl 4), triphenyl sulfonium triflat (TPS) and tetrabutylammonium hydroxide(TBAH). The solvent used was propylene glycol methyl ether acetate. The compositions are as below:

Table 3

| resist No. | solid content | TPS | TBAH |
|---|---|---|---|
| a1 | 22% | 3% | 0.9% |
| a2 | 22% | 1.5% | 0.45% |
| a3 | 22% | 1% | 0.15% |

The above resists were coated on HMDS treated Si wafers by spin coating at a spin speed of 3000 rpm. The thickness of the resist films were around 10.30 KÅ after post apply bake at 90 C for 5 minutes. The coated wafers were exposed to DUV radiation through a chrome mask on a Canon 0.37NA Excimer Laser Stepper at 248nm, and then all developed with 0.18N tetramethyl ammonium hydroxide (TMAH) developer for 90s. No post exposure bake was introduced in this experiment. The film thickness loss after this develop process was around 300 Å. The nominal dose for both resist a1 and a2 was the same (around 32 mJ) to resolve 0.5 and 0.45 μm images. However, with less TBAH/TPS ratio, resist a3 had a nominal dose around 23 mJ.

## Example 16

Resist sensitivity as a function of MOP protection.

Four sets of resists were formulated with the PHMOP synthesized in Example 1 & 2 or with similar procedures.

Table 4

| Resist No. | MOP/PHS | Litho. Dose | %TPS | %TBAH |
|---|---|---|---|---|
| b1 | 27.4 | 14 mj | 1.0 | .17 |
| b2 | 23.4 | 16 mj | 0.7 | 0.14 |
| b3 | 19.3 | 17 mj | 0.75 | 0.15 |
| b4 | 10.5 | 18 mj | 0.8 | 0.2 |

The processes used for these resists were very similar to Example 15. The solid contents were around 20%. The post apply bake was 95 C for 2 min. and the develop condition was 0.15 N TMAH for 60s. For b1 the developer concentration was 0.21 N. The lithographic doses used above were obtained from the doses which yielded images with the nominal linewidth of 0.45 μm.

## Example 17

Resist using MDT as photoacid generator.

A resist was formulated with 2.5% butylated hydroxytoluene and 10% MDT in PHMOP (synthesized in Example 3), and dissolved in PMA to give a total solid content of 20%. The resist was coated on HMDS treated Si wafer and exposed to a DUV radiation through a chrome mask on a Canon 0.37NA Excimer Laser Stepper at 248nm. The resist gave 0.4 μm positive images with vertical sidewalls at a dose of 9mj after developing with 0.14 N TMAH for 45 s. The film thickness loss during development was less than 400 Å.

## Example 18

Resist using 1,2,3,-tris(4-Fluorobenzenesulfonyloxy)benzene (FBS) as photoacid generator.



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A resist was formulat d with 5% FBS and 0.2% TBAH in PHMOP (synthesized similar to that of lot #3 in Example 1) and dissolved in PMA to give a total solid content of 20%. The resist was coated on HMDS treated Si wafer and exposed to DUV radiation through a chrome mask on a Canon 0.37NA Excimer Las r Stepper at 248nm. The resist gave 0.45 μm positive images with vertical sidewalls at a dose of 64mj after development with 0.18 N for 70s., The film lost during this process was less than 400 Å. When the FBS loading and development time were changed to 10% and 60 s respectively, the resist gave 0.40 μm positive images with vertical sidewalls at a dose of 56mj.

Example 19

Deep-UV Lithography of Resist using Benzenesulfonyl benzoyldiazomethane (BSPDM) as photoacid generator.

A resist was formulated with 2% BSPDM and 0.25% TBAH in PHMOP (lot #7 in Example 2) and dissolved in PMA to give a total solid content of 20%. The resist was coated on HMDS treated Si wafer and exposed to a DUV radiation through a chrome mask on a Canon 0.37NA Excimer Laser Stepper at 248nm. The resist gave 0.40 μm positive images with nearly vertical sidewalls at a dose of 36mj after development with 0.15 N for 90s.

Example 20

N-methyl pyrrolidinone contamination test

A resist formulated as in Example 18 was coated and exposed to saturated N-methyl pyrrolidinone (NMP) vapor for 255s and was processed as in example 18. No linewidth change on the resolved images was observed compared with those of the wafer without NMP exposure. No T-top was found on the resolved images. At the same time, a resist of t-butylcarbonate functionalized system was exposed to the same NMP vapor pressure for 45s. The resist images showed T-tops with significant change in linewidth and were not fully developed. Another formulation with 0.7% TPS and 0.14% TBAH in the same PHMOP (as Example 18) polymer matrix showed the same resilience to NMP; no change in image size after 255 s NMP exposure.

Example 21

Lithography of lot #6 in Example 2.

A resist was formulated with 0.75% TPS and 0.15% TBAH in PHMOP (synthesized in Example 2 lot #6) and dissolved in PMA to give a total solid content of 20%. The resist was coated on several HMDS primed silicon wafers and baked at 100 deg C for 120s on a hot plate. One coated wafer was exposed to DUV radiation through a chrome mask on a Canon 0.37NA Excimer Laser Stepper at 248nm and received a dose of 18 mJ/cm$^2$. The exposed wafer is then developed in 0.15 N aqueous TMAH for 60 seconds which provided 0.4 μm positive images with nearly vertical sidewalls.

Example 22

Process with post exposure bake.

A coated wafer from example 21 was exposed to DUV radiation, receiving a 16 mJ/cm$^2$ dose followed by a PEB at 90° C for 90 sec, and development in 0.15 N TMAH for 60 seconds. 0.35 μm positive images were obtained having nearly vertical sidewalls.

Example 23

Linewidth stability with long expose-develop delay

Another one of the exposed wafers of example 21 was stored under ambient condition for 24 hours before development in TMAH for 60 seconds. 0.4 μm positive images with linewidth within 10% of that from example 21 were produced.

Example 24

Linewidth stability with long expose-PEB delay

Another one of the exposed wafers of example 21 was stored under ambient environment for 24 hours before a 90 seconds PEB at 90 °C and development in TMAH for 60 seconds. 0.35 μm positive images having



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near vertical sidewalls were produced. The linewidth measurements of images were within 10% of that obtained in example 22.

Example 25

Effect of different post exposure bake temperature on the linewidth of resist image.

A resist formulation was obtained with the following compositions: 0.15% TBAH, 0.75% TPS and PHMOP (as synthesized in Example 2 lot #6) to make up 20% solid in PMA. The resist was coated on HMDS primed Silicon wafers and baked at 100 deg C for 120s on a hot plate. The coated wafers were exposed to a DUV radiation through a chrome mask on a Canon 0.37NA Excimer Laser Stepper at 248nm and received a dose of 18 mJ/cm². Except for one wafer which was not subjected to any heat treatment, the rest of exposed wafers were subjected to a series of different baking temperatures respectively for 90s without any PEB delay. The exposed wafers were then developed in aqueous 0.15N TMAH for 60 seconds right after PEB. The linewidth for 0.4 μm resist images measured for each wafer at each temperature are summarized as below: 0.39 μm for no bake, 0.36 μm for 50 °C PEB, 0.38 μm for 60 °C, 0.37 μm for 70 °C, 0.38 μm for 80 °C, 0.39 μm for 90 °C and 0.38 μm for 102 °C respectively. It was found that some extra resist thinning occurred if the PEB applied to the resist was above 100 °C.

Example 26

Polymer bound diazoacetoacetate (DZA) as a photo-carboxylic acid generator in Deep-UV lithography

A resist was formulated with 16-18% of the acid generator DZA (based on total solids) and PHMOP in PMA to give a total solids content of 20%. The resist was coated on HMDS treated Si wafer and exposed to DUV radiation through a chrome mask on a Canon 0.37NA Excimer Laser Stepper at 248 nm. The resist had a sensitivity of 16-20 mJ/cm² and has a linear resolution down to 0.4 μm lines and spaces. The post exposure bake was 80 °C for 90 s and the developer was 0.14 N TMAH. The 2 component resist was stable to NMP up to 5 minutes, without any deterioration to profiles and had a shelf life in solution of at least 2 months at room temperature.

Example 27

Sensitivity as a function of MOP protection during e-beam exposure.

Resist was made by mixing PHMOP of examples 1 & 2 with 0.7% TPS and 0.14% TBAH in PMA to yield 20% solid content solution. The resists were spin coated on HMDS primed wafers. The coated film then was baked on a hot plate at 110°C for 3 min. The exposure was performed on a 50 Kev e-beam exposure tool (Hontas tool). The wafers then were stored in a nitrogen box for at least half an hour before developing in 0.14N TMAH aqueous developer for 50 sec. Contrast curves were constructed for each resist and the images were examined with an SEM. All resists were capable of resolving line and space pairs down to 0.20 μm with reasonably vertical profiles. The resist sensitivity to first order is not affected by the MOP protection as much as by the variation in acid generator and stabilizing base loadings. However, the effect of MOP protection was evident from the film thickness loss during development; the lower the MOP protection the higher film thickness loss.

Example 28

Sensitivity as a function of TPS and TBAH loadings during e-beam exposure.

Resist was made by mixing lot#5 of example 1 with different loadings of TPS and TBAH in PMA. The resists were spun coated on HMDS primed Si wafers. A PAB of 110°C for 3 min was carried out before exposure to e-beam from a 50KV Hontas tool. The wafers were developed in 0.14N TMAH for 50 sec after at least half an hour delay. The resist sensitivity is significantly affected by the base loading and residual methanol from it; increased amount of base or methanol leads to decrease in resist sensitivity. The effect of TPS loading when combined with the base is less significant when compared to TPS without base. Furthermore, this example shows the extreme sensitivity of the resist to trace amounts of acid.

Example 29

R sist Shelf Life

The extreme sensitivity observed in Example 1 and 2 of the resist formulation to small amounts of acid



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raised a question about the resist's shelf life. Two approaches have been used to stabilize the resist and xtend its shelf life. The first is by adding a bas to the resist and the second is by purifying the solvent and minimizing its residual acid content. Both approaches showed an improvement in shelf life. However, more gain in shelf life was attained by purifying the solvent. The shelf life was examined by aging the resist material in a constant temperature bath at 40 C. Both the resist dissolution rate in 0.21N TMAH and its sensitivity were monitored as a function of time in the bath. The effect of aging manifested itself by changing the dissolution rate which is correlated to MOP deprotection. The resist sensitivity is slightly affected by the aging process.

Example 30

I-line Lithography
Chemical amplification with carboxylic acid generated from diazonaphthoquinone system.

A resist containing PHMOP synthesized in Example 3 and 10 Wt.% of p-creol ester of 2-diazo-1-naphthalene-4-sulfonic acid was formulated in propylene glycol methyl ether acetate with the solid content at 20%. The resist was spin coated at 3000 rpm on an HMDS treated Si wafer and post apply baked at 90°C for 5 minutes. After exposure to 365 nm radiation with a GCA stepper (0.35 NA) for 0.5 s (approximately 50 mj), the resist was baked at 88 °C for 90s and developed with 0.15 N TMAH for 60 s. An image resolution down to 0.6 μm was obtained. It appeared to exhibit no or very little chemical amplification when T-butyl carbonate protected polyhydroxystyrene with this DQ compound was used, which is evident from the lack of a sharp latent image after post exposure bake and the failure to resolve small image even at much higher dose.

Example 31

I-line lithography using 2-methoxypropyl protected compounds in a three component system.

The photoresist solution for I-line exposure (365 nm) was formulated from 4 parts by weight of one of the 2-methoxy propyl protected compounds synthesized in Examples 12 & 13, 2 parts by weight of the photoacid generator, 14 parts by weight of novolak resin and 80 parts by weight of the solvent propylene glycol monomethyl ether acetate. This solution was spun coated to a thickness of 1.08 μm on silicon wafers and post apply baked at 90 °C for 90 s. The resist was then patterned by the exposure at 0.8-1.0 s on GCA (0.35 NA) stepper and post exposure baked at 100-110 °C for 60 s followed by the development in 0.263 N TMAH.

Example 32

X-ray lithography

A resist was formulated with 1% TPS and 0.2% TBAH in PHMOP (Example 1 lot #3) and dissolved in PMA to give a total solid content of 20%. The resist was spin coated on HMDS primed Si wafer and received a PAB at 100° C for 2 minutes. Exposure was carried out on a RDY stepper attached to an Oxford Synchrotron radiation compact ring located at the IBM EF facility. The dose was varied by changing the scan speed to generate a contrast curve. The wafers were developed in 0.15 N TMAH for 60 seconds. The resist exhibited a reasonable contrast and a dose to clear of about 100 mj. Further process development may be required to optimize resist contrast and image control, nevertheless this example demonstrates feasibility of using this resist for X-ray lithography.

Upon a reading of the present disclosure, it will be apparent to the skilled artisan that other embodiments of the present invention beyond those embodiments specifically described herein may be made or practiced without departing from the spirit of the invention. Similarly, changes, combinations and modifications of the presently disclosed embodiments will also become apparent. The embodiments disclosed and the details thereof are intended to teach the practice of the invention and are intended to be illustrative and not limiting. Accordingly, such apparent but undisclosed embodiments, changes, combinations, and modifications are considered to be within the spirit and scope of the present invention as limited solely by the appended claims.

## Claims

1. An aqueous base developable microlithographic resist composition comprising in admixture:
   (a) a film forming polymer having recurrent hydroxyl groups chemically linked thereto,
   (b) an acid labile compound comprising a ketal moiety, and
   (c) an acid generating compound which forms an acid upon exposure to actinic radiation,

   wherein the acid generated upon exposure causes the cleavage of at least a portion of said compound



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comprising a ketal moiety and wherein the exposed composition is rendered selectiv ly more soluble in aqueous base compared to the unexposed composition.

2. The composition of claim 1 wherein at least a portion of the film forming polymer hydroxyl groups are O-substituted with said acid labile compound comprising a ketal moiety, and wherein the degree of O-substitution is in the range from about 5% to about 100%.

3. The composition of claim 1 wherein the film forming polymer having recurrent hydroxyl groups further comp rises hydroxyaromatic groups.

4. The composition of claim 1 wherein the film forming polymer having recurrent hydroxyl groups is the condensation reaction product of a substituted or unsubstituted phenol with an aldehyde.

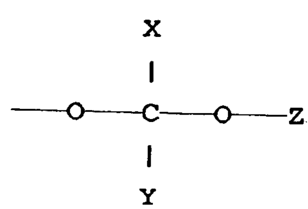
5. The composition of claim 4 wherein the hydroxyaromatic polymer is the condensation reaction product of formaldehyde with phenol or an alkylphenol.

6. The composition of claim 1 wherein the hydroxyaromatic polymer is a polymer selected from the group consisting of polymers and copolymers derived from a substituted or unsubstituted hydroxystyrene and polysilsesquioxanes having hydroxyaromatic groups chemically linked thereto.

7. The composition of claim 6 wherein the hydroxyaromatic polymer is polyhydroxystyrene.

8. The composition of claim 6 wherein the hydroxyaromatic polymer is a copolymer derived from a substituted or unsubstituted hydroxystyrene and a cyclic alcohol of the form
where X is, independently, a hydrogen or an alkyl group having 1 to 8 carbons, and m is in the range of about 0.8 to 1, and n is in the range of about 0 to 0.2.

9. The composition of claim 1 wherein said acid labile compound comprising a ketal moiety further comprises a compound of the form



wherein X, Y, and Z, are selected, independently, from the group consisting of non-bridging alkyl, aryl, alicyclic, and O-heterocyclic groups, and bridging groups comprising 2 to 8 carbons between any two of X, Y, and Z.

10. The acid labile compound of claim 9 wherein the ketal moiety is selected from the group consisting of 2-(2-methyl-tetrahydrofuranyl)oxy, 2-(2-methyl-tetrahydropyranyl)oxy, 1-(1-methoxycyclohexyl)oxy, 2-(2-methoxypropyl)oxy, 4-(4-methoxy-tetrahydropyranyl)oxy, and (1-phenoxy-1-phenylethyl)oxy.

11. The acid labile compound of claim 10 wherein the ketal moiety is 2-(2-methoxypropyl)oxy.

12. The composition of claim 1 wherein the acid generating compound is selected from the group consisting of metallic, metalloid, and non-metallic onium salts, aryl sulfonates, 2-nitrobenzyl esters, beta-ketosulfones, disulfones, bis-arylsulfonyl diazomethanes, alpha-keto diazides, alpha-carboxyl diazides, precursors of substituted and unsubstituted sulfonic acids, and diazonapthoquinones.

13. The composition of claim 1 wherein the acid generating compound is chemically linked to a polymer.

14. The composition of claim 13 wherein the acid generating compound is a polymer having hydroxyl groups, and wherein at least a portion of the hydroxyl groups are O-substituted with substituted or unsubstituted diazoacetoacetate ester groups.



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15. The composition of claim 1 additionally comprising a residual acid scavenger.

16. The composition of claim 15 wherein the r sidual acid scavenger is selected from the group consisting of t traalkylammonium hydroxides, tetraalkanol ammonium hydroxides, dimethylaminopyridines, and ethylene oxide / propylene oxide block copolymer surfactants.

17. The composition of claim 1 additionally comprising a surfactant.

18. The composition of claim 1 additionally comprising a dye.

19. The composition of claim 18 wherein the dye absorbs energy from actinic radiation having one or more wavelengths in the range from about 180 nm to about 400 nm and said dye transfers absorbed energy to the acid generating compound to form an acid.

20. The composition of claim 18 wherein the dye is selected from the group consisting of 9-anthracenemethanol, 9-phenoxymethylanthracene, 9,10-diphenylanthracene, substituted phenanthracenes, substituted biphenyls, substituted and unsubstituted 4-phenylazoresorcinol, crystal violet base, and coumarin dyes.

21. The composition of claim 1 additionally comprising a solvent.

22. The method for forming a microlithographic relief image comprising the steps of
applying, to a microlithographic substrate, a radiation sensitive thin film of the composition according to claim 1,
patternwise exposing the radiation sensitive thin film to form a latent image, and
developing the latent image to form a relief image in the thin film.

23. The method of claim 22 wherein the radiation sensitive thin film is patternwise exposed to radiation from an electron beam, ion beam, ultraviolet, or x-ray source.

24. An acid sensitive polymeric composition comprising the ketal reaction product of a polymer having recurrent hydroxyl groups chemically linked thereto and a reactant selected from the group consisting of substituted vinyl ethers and ortho esters.

25. An acid sensitive polymeric composition comprising the ketal reaction product of a transetherification reaction between a ketal and a polymer having recurrent hydroxyl groups chemically linked thereto.



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European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 94 48 0046

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.5) |
|---|---|---|---|
| X | EP-A-0 520 654 (HOECHST CELANESE CORPORATION) | 1,3,6,7, 9,12, 17-23 | G03F7/004<br>G03F7/039 |
| Y | * page 10, line 9 *<br>* page 11, line 1 - line 2; claims 1,7,11,15,25; example 8 *<br>--- | 4,5 | |
| X,D | EP-A-0 520 642 (WAKO PURE CHEMICAL INDUSTRIES LTD) | 2,10,11, 24 | |
| Y,D | * page 8 - page 9 *<br>* page 10, line 16 - line 18 *<br>* page 10, line 35 - line 44 *<br>* page 16, line 21; examples 9,22,26; table 1 *<br>--- | 25 | |
| Y | EP-A-0 432 599 (BASF AKTIENGESELLSCHAFT)<br>* page 5, line 26 - line 36 *<br>* page 6, line 35 - line 49 *<br>* page 7, line 12 - line 55 *<br>--- | 4,5,25 | |
| X | EP-A-0 372 408 (BASF AKTIENGESELLSCHAFT)<br><br>* page 3, line 6 *<br>* page 6, line 30 - line 40; claims *<br>--- | 1,3,6,7, 9,12,18, 19,21-23 | TECHNICAL FIELDS SEARCHED (Int.Cl.5)<br>G03F |
| A | PATENT ABSTRACTS OF JAPAN<br>vol. 013, no. 347 (P-910) 4 August 1989<br>& JP-A-01 106 037 (MATSUSHITA ELECTRIC IND CO LTD) 24 April 1989<br>* abstract *<br>----- | 13,14 | |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 3 October 1994 | J.-M. DUPART |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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